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TITLE: Hollow fiber **membrane** contactor

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PARENT-CASE:

CROSS-REFERENCE TO RELATED APPLICATIONS

This application is a continuation of application Ser. No. 09/889,960, filed Jul. 24, 2001, now U.S. Pat. No. 6,582,496, which claims priority from the U.S. National Phase of International Application No. PCT/US00/02378, filed Jan. 28, 2000, which designated the United States and was published in the English language as WO 00/44479 on 03 Aug. 2000. The PCT Application claims priority from U.S. provisional application Ser. No. 60/117,932, filed Jan. 29, 1999.

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FIELD-OF-CLASSIFICATION-SEARCH: 95/45; 95/46 ; 96/6 ; 96/8 ; 96/10 ; 96/14
See application file for complete search history

REF-CITED:

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PAT-NO	ISSUE-DATE	PATENTEE-NAME	US-CL		
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PRIMARY-EXAMINER: Spitzer; Robert H.

ABSTRACT:

A fully perfluorinated thermoplastic hollow fiber **membrane** fluid-fluid contactor and a process for manufacturing the contactor is described. The contactor has a unitary end structure produced by a single step potting and bonding process. The contactor can be operated with low surface tension liquids and in harsh chemical environments.

12 Claims, 5 Drawing figures

Exemplary Claim Number: 1

Number of Drawing Sheets: 5

Abstract Text - ABTX (1):

TITLE - TI (1):

Hollow fiber **membrane** contactor

Brief Summary Text - BSTX (2):

This invention relates to a hollow fiber **membrane** contactor for phase separations and other phase contact applications. The contactor is made from perfluorinated thermoplastic polymeric materials, has a high packing density providing high useful contacting area, and the ability to operate with liquids of low surface tension.

Brief Summary Text - BSTX (5):

Conventional contactors have several deficiencies. Primary among these is the fact that the individual gas and liquid flows cannot be varied independently over wide ranges. Tray columns are prone to such problems as weeping at low gas flows and flooding at high liquid flows. Packed towers can flood at high flow rates. The use of low liquid flow rates In a packed tower would lead to channeling and reduced effective surface area. Excessive frothing or foam formation can lead to process inefficiency. Wetted wall contactors have inherently low mass transfer coefficients, and can flood at high gas flow rates. The development of **membrane** contactors has overcome these deficiencies.

Brief Summary Text - BSTX (6):

 Membrane contactors are devices through which two fluid phases flow separated by a **membrane** permeable to the gas being transferred. If a microporous **membrane** is being used, the preferred method relies on the non-wetting characteristic of the **membrane** material and the pore size to prevent liquid from intruding into the pores and filling them. Gas transfer then occurs through the gas filled pores to or from the liquid, depending on whether the process is absorption or stripping. If a non-porous **membrane** is used, gas transfer is controlled by the diffusion rate in the non-porous **layer of the membrane**. In some cases, such as oxygen removal from ultrapure water, gas stripping is done with a vacuum instead of a stripping gas flow. While other **membrane** geometries are available for this use, hollow fiber **membranes** are ideally suited as contactors.

Brief Summary Text - BSTX (7):

 A hollow fiber porous **membrane** is a tubular filament comprising an outer diameter, an inner diameter, with a porous wall thickness between them. The inner diameter defines the hollow portion of the fiber and is used to carry one of the fluids. For what is termed tube side contacting, the liquid phase flows through the hollow portion, sometimes called the lumen, and is maintained separate from the gas phase, which surrounds the fiber. In shell side contacting, the liquid phase surrounds the outer diameter and surface of the fibers and the gas phase flows through the lumen.

Brief Summary Text - BSTX (8):

 The outer or inner surface of a hollow fiber **membrane** can be skinned or unskinned. A skin is a thin dense surface **layer** integral with the substructure of the **membrane**. In skinned **membranes,** the major portion of resistance to flow through the **membrane** resides in the thin skin. The surface skin may contain pores leading to the continuous porous structure of the substructure, or may be a non-porous integral film-like surface. In porous skinned **membranes,** permeation occurs primarily by connective flow through the pores. Asymmetric refers to the uniformity of the pore size across the thickness of the **membrane**; for hollow fibers, this is the porous wall of the fiber. Asymmetric **membranes** have a structure in which the pore size is a function of location through the cross-section, section, typically, gradually increasing in size in traversing from one surface to the opposing surface. Another manner of defining asymmetry is the ratio of pore sizes on one surface to those on the opposite surface.

Brief Summary Text - BSTX (9):

 Manufacturers produce **membranes** from a variety of materials, the most general class being synthetic polymers. An important class of synthetic polymers are thermoplastic polymers, which can be flowed and molded when heated and recover their original solid

properties when cooled. As the conditions of the application to which the **membrane** is being used become more severe, the materials that can be used becomes limited. For example, the organic solvent-based solutions used for wafer coating in the microelectronics industry will dissolve or swell and weaken most common polymeric **membranes**. The high temperature stripping baths in the same industry consist of highly acid and oxidative compounds, which will destroy **membranes** made of common polymers. Perfluorinated thermoplastic polymers such as poly(tetrafluoroethylene-co-perfluoro (alkylvinylether)) (poly(PTFE-CO-PFVAE)) or poly(tetrafluoroethylene-co-hexafluoropropylene) (FEP) are not adversely affected by severe conditions of use, so that **membranes** made from these polymers would have a decided advantage over ultrafiltration **membranes** made from less chemically and thermally stable polymers. These thermoplastic polymers have advantages over poly(tetrafluoroethlene) (PTFE), which is not a thermoplastic, in that they can be molded or shaped in standard type processes, such as extrusion. Perfluorinated thermoplastic hollow fiber **membranes** can be produced at smaller diameters than possible with PTFE. Fibers with smaller diameters, for example, in the range of about 350 micron outer diameter to about 1450 micron outer diameter, can be fabricated into contactors having high **membrane** surface area to contactor volume ratios. This attribute is useful for producing compact equipment, which are useful in applications where space is at a premium, such as in semiconductor manufacturing plants.

Brief Summary Text - BSTX (10):

Being chemically inert, the Poly (PTFE-CO-PFVAE) and FEP polymers are difficult to form into **membranes** using typical solution casting methods as they are difficult to dissolve in the normal solvents. They can be made into **membranes** using the Thermally Induced Phase Separation (TIPS) process. In one example of the TIPS process a polymer and organic liquid are mixed and heated in an extruder to a temperature at which the polymer dissolves. A **membrane** is shaped by extrusion through an extrusion die, and the extruded **membrane** is cooled to form a gel. During cooling the polymer solution temperature is reduced to below the upper critical solution temperature. This is the temperature at or below which two phases form from the homogeneous heated solution, one phase primarily polymer, the other primarily solvent. If done properly, the solvent rich phase forms a continuous interconnecting porosity. The solvent rich phase is then extracted and the **membrane** dried.

Brief Summary Text - BSTX (11):

Hydrophobic microporous **membranes** are commonly used for contactor applications with an aqueous solution that does not wet the **membrane**. The solution flows on one side of the **membrane** and a gas mixture preferably at a lower pressure than the solution flows on the other. Pressures on each side of the **membrane** are maintained so that the

liquid pressure does not overcome the critical pressure of the **membrane,** and so that the gas does not bubble into the liquid. Critical pressure, the pressure at which the solution will intrude into the pores, depends directly on the material used to make the **membrane,** inversely on the pore size of the **membrane,** and directly on the surface tension of the liquid in contact with the gas phase. Hollow fiber **membranes** are primarily used because of the ability to obtain a very high packing density with such devices. Packing density relates to the amount of useful **membrane** surface per volume of the device. It is related to the number of fibers that can be potted in a finished contactor. Also, contactors may be operated with the feed contacting the inside or the outside surface, depending on which is more advantageous in the particular application. Typical applications for contacting **membrane** systems are to remove dissolved gases from liquids, "degassing", or to add a gaseous substance to a liquid. For example, ozone is added to very pure water to wash semiconductor wafers.

Brief Summary Text - BSTX (12):

Porous contactor **membranes** are preferred for many applications because they will have higher mass transfer than nonporous **membranes**. For applications with liquids having low surface tensions, smaller pore sizes will be able to operate at higher pressures due to their resistance to intrusion. Non-porous contactor **membranes** are preferred in cases where the liquid vapor pressure is high, or where high temperature operation increases the vapor pressure. In these cases, evaporation through a porous **membrane** may result in substantial liquid loss. Non-porous **membranes** may also be preferred in high-pressure applications, where intrusion of a porous **membrane** would be a problem.

Brief Summary Text - BSTX (13):

Membrane contactors can also be useful in applications where in addition to phase transfer of a species from a feed stream to a second phase, a chemical reaction is desired between that species and a second reactant in the second phase. **Membrane** contactors would provide high surface area for mass transfer and maintain the product separate from the feed stream.

Brief Summary Text - BSTX (14):

Z. Qi and E. L. Cussler (J. **Membrane** Sci. 23(1985) 333-345) show that **membrane** resistance controls absorption of gases such as ammonia, SO.sub.2 and H.sub.2 S in sodium hydroxide solutions. This seems generally true for contactors used with strong acids and bases as the absorption liquid. For these applications, a more porous contactor **membrane,** such as a microporous **membrane,** would have an advantage, because the **membrane** resistance would be reduced. This would be practical if the liquid does not intrude the pores and increase resistance. With the very low surface tension materials used in the present invention, this would be possible without coating the surface of the

fibers with a low surface tension material, which is an added and complex manufacturing process step.

Brief Summary Text - BSTX (15):

 Membrane contactors have several advantages over conventional equipment. **Membrane** contactors have a higher surface area per unit volume than conventional packed towers. More importantly, **membrane** contactors are not disturbed by high or low flow rates and do not suffer from the problems set forth above for conventional contactors. This is due to the fact that in **membrane** contactors, the flow rates can be controlled independently because the separate phases are not in-physical contact and cannot influence each others flow. **Membrane** contactors also have the advantage that bubbles are not formed in the liquid stream under proper operating conditions. These advantages are useful in important applications.

Brief Summary Text - BSTX (16):

Ozone treatment of drinking water is being increasingly considered. Ozone has the capability of eliminating all viruses, and does not form substances such as trihalomethanes, which are by-products of chlorine treatment and natural substances such as humic or fulvic acids which may be present. For applications requiring a compact apparatus, such as at remote sites, the higher efficiency of a **membrane** contactor would be preferable to the typical small bubble diffuser, which requires significant water-ozone depth to be effective.

Brief Summary Text - BSTX (20):

In U.S. Pat. No. 5,464,480, preferably, the bubbles that are provided by the diffuser are initially about 25 to about 40 microns in diameter. The gas diffuser preferably is made from a mixture of polytetratluoroethylene (PTFE) and perfluoroalkoxylvinylether. By varying the temperature and pressure under which the mixture is prepared by methods known in the art, both porous and nonporous members are formed. The impermeable and permeable members are preferably comprised of about 95% PTFE and about 5% perfluoroalkoxylvinylether. The permeable member and the impermeable member may be joined by any number of methods as long as the result is a **composite** member that will not come apart under the stresses in the tank. Preferably, the members are heat sealed together, essentially melting or fusing the members together using carbon-carbon bonds. Once the permeable member is formed, a trench is bored out of the PTFE in the top portion of the member. The resulting diffuser has on the order of about 100,000 pores of a size of about 25 to about 40 microns in diameter through which gas may permeate into the treatment tank. The use of the french in the diffuser allows the gas to diffuse into the tank as very fine bubbles. In applications for the semiconductor manufacturing industry, a device that supplied homogeneous bubble free ozone dissolved in ultrapure

water would provide more efficient oxidation reactions because the reaction would not be localized at the bubbles. The more homogeneous solution would provide for a more uniform cleaning reaction. Furthermore, the high surface area to volume ratio inherent in hollow fiber devices would give a compact system, suitable for semiconductor operations.

Brief Summary Text - BSTX (22):

U.S. Pat. No. 5,670,094 provides an oxidized water producing method in which a pressurized ozone gas is generated by an electric discharge type ozonator is dissolved in water to be treated through a hollow fiber **membrane,** characterized in that the water pressure inside the **membrane** is maintained higher than the pressure of the ozone gas supplied to the outside of the hollow fiber **membrane** to prevent tiny bubbles and impurities from getting mixed into the water being treated, and the ozone concentration in the treated water is controlled on the basis of the concentration of the ozone gas. This method reference discloses only PTFE **membranes** and does not contemplate the use of an all perfluorinated thermoplastic contactor.

Brief Summary Text - BSTX (23):

Commercially available all PTFE hollow tube contactors are referred to as "hollow tubes", probably because they are relatively large. Patent JP7213880A discloses the fiber manufacturing process for making **composite** PTFE hollow tubes for ozonizing applications. The first step of this process involves extruding PTFE paste derived from a mixture of PTFE powder and lubricants. After the tube is formed, the lubricants are extracted and the powder sintered into a slightly porous PTFE solid tube. The tube is then stretched longitudinally to

Brief Summary Text - BSTX (24):

make it porous. This is different than typical PTFE flat sheet **membranes** made by a similar process. To generate really fine microporous structures, characterized by a node to fibrils network, most PTFE **membranes** are made by biaxial stretching. For hollow fibers, the equivalent process would have been stretching the fiber radially. Probably because of the impracticality of such a step, this radial stretching step is missing from the disclosed process. Consequently, the pores in this tube are only "half-formed", i.e. it did not attain the "node to fibril network" of flat sheet **membrane**. To compensate for this deficiency, the tube underwent a second step of laminating a regular microporous flat sheet **membrane** on top of the external surface of the porous tube. This step involves lamination of a long narrow strip of PTFE microporous **membrane** spirally on the surface of the tubing. This is a tedious, labor intensive process. Also, with the **membrane** laminated to the outside of the hollow tube, the resistance to mass transfer in tube-side flow could be higher in cases were the fluid partially intrudes into the **support**

layer. This arrangement diminishes the potential of using the **membrane** as the barrier for separating the two fluid phases. These deficiencies are overcome with the hollow fiber **membranes** of the present invention.

Brief Summary Text - BSTX (25):

An advantage for contacting applications is that the very low surface tension of these perfluorinated polymers allows use with low surface tension liquids. For example, highly corrosive developers used in the semiconductor manufacturing industry may contain surface tension reducing additives, such as surfactants. These developers could not be degassed with typical microporous **membranes** because the liquid would intrude the pores at the pressures used and permeate, causing solution loss and excess evaporation. In addition, liquid filling the pores would greatly add to the mass transfer resistance of gas transport. U.S. Pat. No. 5,749,941 describes how conventional hollow fiber **membranes** of polypropylene or polyethylene cannot be used in carbon dioxide or hydrogen sulfide absorption into aqueous solutions containing an organic solvent without the use of a solution additive to prevent leakage. While polytetrafluoroethylene (PTFE) **membranes** would work in these applications, presumably because of their lower surface tension, they are difficult to process into hollow fibers. The **membranes** of the present invention are made from polymers having similar surface tension properties to PTFE and are more readily manufactured into small diameter hollow fiber **membranes**.

Brief Summary Text - BSTX (26):

WO 9853894 describes a process of forming compact, high flux, fouling resistant gas filters by coating continuous ultra thin **layer** of non-porous gas permeable polymer over filter surface by contacting one side of microporous substrate with dilute coating solution of polymer, preferably amorphous copolymer of **perfluoro-2,2-dimethyl-1,3-dioxole,** which is hydrophobic and oleophobic. Substrate pore size filters polymer from solution as solvent flows through, leaving ultra thin **layer** of polymer. Process is useful to coat sheet and hollow fiber substrates, particularly multiple hollow fibers assembled in modules. These **membranes** have been described as useful for contactor applications. (S. Nemser, Paper presented at 1998 North American **Membrane** Society Meeting.) This method requires a separate and complex coating step to produce a non-porous contactor fiber. Furthermore, a fully perfluorinated thermoplastic contactor is not described.

Brief Summary Text - BSTX (28):

In a first embodiment of the present invention, a highly asymmetric perfluorinated thermoplastic hollow fiber is used as the barrier. The **membrane** is comprised of a skinned surface on one diameter, and a porous surface on the other diameter. The smaller pored skinned surface of the asymmetric **membrane** is designed to face the liquid flow and offer the highest resistance to liquid intrusion. The thin skin offers low diffusional

resistance, yet the small pores offer the highest intrusion resistance. Also, the perfluorinated surface has low interfacial energy, which further increases the resistance to liquid intrusion.

Brief Summary Text - BSTX (29):

In a second embodiment, a perfluorinated thermoplastic microporous hollow fiber **membrane** is used as the barrier. These **membranes** are useful in applications where the **membrane** resistance to mass transfer may be controlling, or liquid intrusion into the pores is a lesser problem.

Brief Summary Text - BSTX (30):

In a third embodiment, the skinned surface of the perfluorinated thermoplastic hollow fiber **membrane** is non-porous.

Brief Summary Text - BSTX (31):

This invention provides for a fully perfluorinated thermoplastic hollow fiber **membrane** contactor with unitary end structures having a high packing density and capable of operating with liquids having interfacial surface tension of greater than about 20 mN/m at 20.degree. C. A manufacturing method for the contactor is provided and described.

Brief Summary Text - BSTX (32):

The contactor is comprised of a bundle of substantially parallel hollow fiber **membranes** potted at both ends and having unitary end structure(s) with the housing containing the fibers. The perfluorinated thermoplastic hollow fiber **membranes** of this invention are made of polymers such as poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)), poly (tetrafluoroethylene-co-hexafluoropropylene), or blends thereof. The contactor has fluid inlets and outlet connections for the two fluids to be contacted. As illustrated in FIG. 1, fluid 1 enters the contactor 2 through the fiber lumens 3 through connection 10, traverses the interior of the contactor while in the lumens, where it is separated from fluid 4 by the **membrane,** and exits the contactor through the fiber lumens at connection 20. Fluid 24 enters the housing through connection 30 and substantially fills the space between the inner wall of the housing and the outer diameters of the fibers, and exits through connector 40.

Brief Summary Text - BSTX (33):

In the first embodiment, the fibers are asymmetric skinned **membranes** having a porous skinned surface on one diameter and a porous surface on the other diameter, with

the fiber wall between comprising a porous structure. The process of making a contactor of the first embodiment from asymmetric skinned perfluorinated thermoplastic polymers uses hollow fiber **membranes** made by the process described in concurrent U.S. patent application 60/117,854, filed Jan. 29,1999, the disclosure of which is incorporated by reference. For use with liquid on the lumen of the fibers, the inner diameter will be made skinned, and for use with liquid on the outer or shell side of the fibers, the outer diameter of the fibers will be made skinned, The potted fibers are spaced closely, without any fiber crossover or fibers impinging on each other so tightly that they can not be forced apart by the liquid or gas flow. For liquid flow in the lumen, which is the preferred mode of operation for liquid-gas contacting, the fibers do not have to be spaced uniformly apart. This simplifies the contactor manufacturing process.

Brief Summary Text - BSTX (34):

In the second embodiment, perfluorinated thermoplastic microporous hollow fiber **membranes** are made by a process disclosed in patent application Ser. No. 60/117,852 filed Jan. 29, 1999, the disclosure of which is incorporated by reference. Equivalent **membranes** made by another process could also be used. Preferred polymers are perfluorinated thermoplastic polymers, more specifically poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) (poly (PTFE-CO-PFVAE)), poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP), or blends of these polymers, which are dissolved in a solvent to give a solution having an upper critical solution temperature, and which when the solution is cooled, separates into two phases by liquid-liquid phase separation. Teflon.RTM. PFA is an example of a poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) in which the alkyl is primarily or completely the propyl group. FEP Teflon.RTM. is an example of poly (tetrafluoroethylene-co-hexafluoropropylene). Both are manufactured by DuPont, Wilmington, Del. Neoflon.TM. PFA (Daikin Industries) is a polymer similar to DuPont's PFA Teflon.RTM.. A poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) polymer in which the alkyl group is primarily methyl is described in U.S. Pat. No. 5,463,006. A preferred polymer is Hyflon.RTM. POLY (PTFE-CO-PFVAE) 620, obtainable from Ausimont USA, Inc., Thorofare, N.J.

Brief Summary Text - BSTX (35):

In a third embodiment, the conditions of **membrane** making of the first embodiment are adjusted to produce a skinned asymmetric **membrane** with a non-porous skin. A preferred method is to increase the amount of polymer used in the solution used to make the **membranes**.

Drawing Description Text - DRTX (2):

FIG. 1. is an illustration of a hollow fiber **membrane** contactor.

Drawing Description Text - DRTX (3):

FIG. 2a. is an illustration of hollow fiber **membrane** wrapped around a frame.

Drawing Description Text - DRTX (4):

FIG. 2b. is an illustration showing a flat rectangular coil of hollow fiber **membrane**.

Detailed Description Text - DETX (2):

The asymmetric skinned hollow fiber **membrane** is produced by the process described in concurrent U.S. patent application Ser. No. 60/117,854 filed Jan. 29,1999, the disclosure of which is incorporated by reference. That process is based on the Thermally Induced Phase Separation (TIPS) method of making porous structures and **membranes**. A mixture of perfluorinated thermoplastic polymer pellets, usually ground to a size smaller than supplied by the manufacturer, from about 100 to about 1000 microns, preferably about 300 microns, more preferably supplied or ground to a powder, and a solvent, such as chlorotrifluoroethylene oligimer, is first mixed to a paste or paste-like consistency. The polymer comprises between approximately 12% to 75%, preferably 30% to 60%, by weight of the mixture. Preferred polymers are perfluorinated thermoplastic polymers, more specifically poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) (poly (PTFE-CO-PFVAE)) or poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP), or blends of these polymers, which are dissolved in a solvent to give a solution having an upper critical solution temperature, and which when the solution is cooled, separates into two phases by liquid-liquid phase separation. PFA Teflon.RTM. is an example of a poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) in which the alkyl is primarily or completely the propyl group. FEP Teflon.RTM. is an example of poly (tetrafluoroethylene-co-hexafluoropropylene). Both are manufactured by DuPont. Neoflon.TM. PFA (Daikin Industries) is a polymer similar to DuPont's PFA Teflon.RTM.. A poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) polymer in which the alkyl group is primarily methyl is described in U.S. Pat. No. 5,463,006. A preferred polymer is Hyflon.RTM. POLY (PTFE-CO-PFVAE) 620, obtainable from Ausimont USA, Inc., Thorofare, N.J.

Detailed Description Text - DETX (3):

The solvent is chosen so the **membrane** formation occurs by liquid-liquid, rather than solid-liquid phase separation when the solution is extruded and cooled. Preferred solvents are saturated low molecular weight polymers of chlorotrifluoroethylene. A preferred solvent is HaloVac.RTM. 60 from Halocarbon Products Corporation, River Edge, N.J. Choice of the solvent is dictated by the ability of the solvent to dissolve the polymer when heated to form an upper critical solution temperature solution, but not to excessively boil at that temperature. Fiber extrusion is referred to as spinning and the

extruded fiber length from the die exit to the take-up station is referred to as the spin line. The paste is metered into a heated extruder barrel where the temperature is raised to above the upper critical solution temperature so that dissolution occurs. For inside skinned hollow fiber **membranes,** the homogeneous solution is then extruded through an annular die directly into a liquid cooling bath with no air gap. The lumen diameter is maintained with a constant pressure of gas. The liquid cooling bath is maintained at a temperature below the upper critical solution temperature of the polymer solution. The preferred bath liquid is not a solvent for the thermoplastic polymer, even at the extrusion temperature. Upon cooling, the heated and shaped solution undergoes phase separation and a gel fiber results. The die tip is slightly submerged for vertical spinning, i.e.; the spin line falls downward, in the direction of a freely falling body. For horizontal spinning, where the spin line exits directly in the horizontal attitude, and is maintained more or less in that plane until at least the first guide roll, a specially design die is used. The die is firmly positioned against an insulated wall with the die tip penetrating through an opening having a liquid-tight seal in the insulator wall. A trough for cooling liquid flow is placed in a recess in the opposite side of the insulating wall, in a manner that will maintain the die nose outlet in a submerged condition. Cooling liquid flows in the trough and overflows in a region of the trough of lesser depth, keeping the die nose outlet submerged with a flow of cooling liquid. In both the vertical and horizontal methods, a booster heater and temperature control means is used to briefly raise the solution temperature at the die tip to prevent premature cooling. In a subsequent step, the dissolution solvent is removed by extraction and the resultant hollow fiber **membrane** is dried under restraint to prevent **membrane** shrinkage and collapse. Optionally, the dried fiber may be heat set at 200.degree. C. to 300.degree. C. Preferably the fiber will be heat set or annealed under restraint at a temperature near the melting temperature of the fiber, which for the preferred polymer of this invention is within a range of from about 270.degree. C. to about 290.degree. C., preferably from about 275.degree. C. to about 285.degree. C., with the most preferred range from about 278.degree. C. to about 282.degree. C. In order to minimize shrinkage during potting, a second, unrestrained, annealing step at similar temperatures is a preferred step. Annealing times for these steps if from about 6 to about 48 hours, more preferably, from about 18 to about 30 hours.

Detailed Description Text - DETX (4):

In the invention described in U.S. Ser. No. 60,117,854, controlled evaporation of solvent from at least one surface of the hollow fiber as it exits the die tip is combined with higher polymer solids solutions and the submerged extrusion process to produce inner diameter skinned asymmetric hollow fiber porous **membranes** from perfluorinated thermoplastic polymers. For this embodiment, the lumen is maintained with a constant pressure of a gas continuously fed into the inner diameter of the lumen. In this embodiment the superheated solvent evaporates inside the lumen as soon as it emerges from the die. The loss of solvent causes a superficial increase in solids concentration on

the inner lumen surface. As the melt is quenched, a very thin skin is formed on the lumen surface, while the rest of the **membrane** forms a microporous structure due to its being submerged in a cooling or quenching bath which prevents the porogen from flashing off the outer surface and prevents the formation of a skin on the outer surface.

Detailed Description Text - DETX (5):

To produce an asymmetric skinned perfluorinated thermoplastic hollow fiber **membrane** with the skin on the outer surface, the process described above is adapted so the lumen is filled with a liquid to prevent evaporation at the inner surface and the outer surface is exposed to the atmosphere in a very short air gap before entering the cooling bath. The lumen-filling liquid can be a liquid that does not boil or excessively vaporize during the extrusion process. Preferred liquids are mineral oil, silicone oil, and dioctylpthlate, with a most preferred liquid being a low molecular weight saturated chlorotrifluorohydrocarbon polymer.

Detailed Description Text - DETX (6):

To produce perfluorinated thermoplastic microporous hollow fiber **membrane,** the teachings of U.S. patent application Ser. No. 60/117,852, filed Jan. 29, 1999, are used. This application provides for high flux, skin-free hollow fiber porous **membranes,** more specifically, microporous **membranes,** from perfluorinated thermoplastic polymers, more specifically poly (tetrafluoroethylene-co-perfluoro (alkylvinylether)) (poly (PTFE-CO-PFVAE)) or poly (tetrafluoroethylene-co-hexafluoropropylene) (FEP) or blends of these polymers.

Detailed Description Text - DETX (7):

A process to produce these **membranes** is provided. The process is based on the Thermally Induced Phase Separation (TIPS) method of making porous structures and **membranes**. A mixture of polymer pellets, usually ground to a size smaller than supplied by the manufacturer, from about 100 to about 1000 microns, preferably about 300 microns, more preferably supplied or ground to a powder and a solvent, such as chlorotrifluoroethylene oligimer, is first mixed to a paste or paste-like consistency. The polymer comprises between approximately 12% to 35% by weight of the mixture. The solvent is chosen so the **membrane** formation occurs by liquid-liquid, rather than solid-liquid phase separation when the solution is extruded and cooled. Preferred solvents are saturated low molecular weight polymers of chlorotrifluoroethylene. A preferred solvent is HaloVac.RTM. 60 from Halocarbon Products Corporation, River edge, N.J. Choice of the solvent is dictated by the ability of the solvent to dissolve the polymer when heated to form an upper critical solution temperature solution, but not to excessively boil at that temperature. Fiber extrusion is referred to as spinning and the extruded fiber length from the die exit to the take-up station is referred to as the spin line. The paste is metered into

a heated extruder barrel where the temperature raised to above the upper critical solution temperature so that dissolution occurs. The homogeneous solution is then extruded through an annular die directly into a liquid cooling bath with no air gap. The liquid cooling bath is maintained at a temperature below the upper critical solution temperature of the polymer solution. The preferred bath liquid is not a solvent for the thermoplastic polymer, even at the extrusion temperature. Upon cooling, the heated and shaped solution undergoes phase separation and a gel fiber results. The die tip is slightly submerged for vertical spinning, i.e.; the spin line falls downward, in the direction of a freely falling body. For horizontal spinning, where the spin line exits directly in the horizontal attitude, and is maintained more or less in that plane until at least the first guide roll, a specially design die is used. The die is firmly positioned against an insulated wall with the die tip penetrating through an opening having a liquid-tight seal in the insulator wall. A trough for cooling liquid flow is placed in a recess in the opposite side of the insulating wall, in a manner that will maintain the die nose outlet in a submerged condition. Cooling liquid flows in the trough and overflows in a region of the trough of lesser depth, keeping the die nose outlet submerged with a flow of cooling liquid. In both the vertical and horizontal methods, a booster heater and temperature control means is used to briefly raise the solution temperature at the die tip to prevent premature cooling. In a subsequent step, the dissolution solvent is removed by extraction and the resultant hollow fiber **membrane** is dried under restraint to prevent **membrane** shrinkage and collapse. Optionally the dried fiber may be heat set at 200.degree. C. To 300.degree. C.

Detailed Description Text - DETX (8):

The potting method is described in concurrent U.S. patent application 60/117,853, filed Jan. 29, 1999, incorporated by reference. This application describes a simplified method for manufacturing a filter element of perfluorinated thermoplastic hollow fiber **membranes** potted with a perfluorinated thermoplastic polymer. The method comprises vertically placing a portion of a bundle of hollow fiber **membrane** lengths with at least one closed, by the closed end, into a temporary recess made in a pool of molten thermoplastic polymer held in a container, holding the fiber lengths in a defined vertical position, maintaining the thermoplastic polymer in a molten state so that it flows into the temporary recess, around the fibers and vertically up the fibers, completely filling the interstitial spaces between fibers with the thermoplastic polymer. A temporary recess is a recess that remains as a recess in the molten potting material for a time sufficient to position and fix the fiber bundle in place and then will be filled by the molten thermoplastic. The temporary nature of the recess can be controlled by the temperature at which the potting material is held, the temperature at which the potting material is held during fiber bundle placement, and the physical properties of the potting material. A temporary recess can also be recess in a solid thermoplastic which will fill when the thermoplastic is heated to a temperature sufficiently above its softening or melting temperature to flow, and held at that temperature for the time necessary to fill the recess.

The end of the fiber can be closed by sealing, plugging, or in a preferred embodiment, by being formed in a loop.

Detailed Description Text - DETX (11):

In a preferred embodiment, the first step of making a (poly (PTFE-CO-PFVAE)) hollow fiber contactor is to wind gel (poly (PTFE-CO-PFVAE)) hollow fibers onto a steel frame to form continuous loops on both sides of the frame. Gel Gel fibers are raw, unextracted fibers with porogen (Halocarbon oil) still embedded in the **membrane** structure. The gel fibers should be substantially parallel to each other. They are spaced closely, yet do not touch or cross each other's paths. The framed fibers are then put into a degreaser to extract the porogens from the **membrane**. After 24 hrs of extraction, the extracted fiber wound frames are put into an oven to anneal the fiber for 24 hrs at a temperature in the range of from about 270.degree. C. to about 290.degree. C., preferably from about 275.degree. C. to about 285.degree. C. the most preferred range from about 278.degree. C. to about 282.degree. C. Since the polymer has a broad melting temperature range, it is sometimes possible to anneal at a temperature slightly higher than the peak or average melting temperature. The fiber frames are retrieved and cooled. After cooling, the fibers are removed from the frame. The looped fiber bundle or bundles are then put back into the oven to anneal for another 24 hrs at the same temperature. The first step anneals the fiber at high temperature under tension, where most of the mechanical properties are set. The second annealing step relaxes the fiber, allowing the fiber to shrink to the equilibrium length with no tension at the annealing temperature. Although the shrinkage is very small, about 5%, this second relaxation step is critical as it prevents shrinkage of the hollow fibers during potting, which would have resulted in non-integral modules.

Detailed Description Text - DETX (15):

In this method, an array of hollow fiber **membranes** may be fabricated by either winding the length of the array upon itself or upon a mandrel. The mandrel, if chosen, is preferably circular in cross section, however other cross sections, such as oval, square, rectangular or polygonal may also be used.

Detailed Description Text - DETX (16):

The wound hollow fiber **membrane** is arranged in a single **layer,** with the windings being substantially parallel to one another either in contiguous contact with, or spaced uniformly apart from, one another. When the appropriate length of hollow fiber **membrane** is accumulated on the mandrel, one or more strips of tape means are applied to the outer surface of the hollow fiber **membrane** segments and positioned along the length of the mandrel in an orientation parallel to its axis of rotation and perpendicular to the central axes of the individual hollow fiber segments. The tape extends from the first

hollow fiber **membrane** segment wound on the mandrel to the least and preferably extends about 1 cm beyond each end of the fiber array. The hollow fiber **membrane** segments are slit along the middle of the entire length of the tape means such that the hollow fiber **membranes** remain joined together by the now halved strip of tape.

Detailed Description Text - DETX (18):

Following the accumulation of approximately a one-half turn of the polymer ribbon extrusions on the tube, the leading edge of the hollow fiber **membrane** array is positioned under and parallel to the tube with the adhesive side of the extended strip of tape means facing the tube. The tape is then brought into contact with the tube outboard of the tubesheets and wound up on the tube. A slight tension is maintained on the hollow fiber array to keep the fibers in contact with the polymer extrusions. Application of the polymer extrusions may be terminated after the entire array is wound about the mandrel. Alternatively, the tubesheets may be built up to a larger diameter depending on the requirements of the rest of the module assembly process. In this case, the rotation of the winding mandrel continues as the molten tubesheets are allowed to cool. The end portions of the sealed fiber bundle can be trimmed to expose the fiber lumens and further machining may be performed to provide a means for sealing the fiber bundle into a suitable housing or the fiber bundle may be contoured to provide details suitable for thermoplastically bonding it to the components of a pressure housing of the same or similar resin material in order to produce a hollow fiber module.

Detailed Description Text - DETX (36):

Samples of hollow fiber **membrane** are soaked in isopropyl alcohol or a mixture of isopropyl alcohol and water, approximately 50% by volume. The wetted sample is then soaked in water to replace the alcohol. The water-wetted sample is held by a tweezers and dipped in a container of liquid nitrogen. The sample is then removed and quickly snapped by bending using a pair of tweezers. Approximately 2 millimeter cut sample is fixed to a sample stub with conductive carbon paint (Structure Probe Inc. West Chester Pa.). Microscopy is done with an ISI-DS130c scanning electron microscope (International Scientific Instruments, Inc, Milpitas, Calif.). Digitized images are acquired by a slow scan frame grabber and stored in. TIF format.

Detailed Description Text - DETX (38):

Preparation of Porous Inner Diameter Skinned Asymmetric Hollow Fiber **Membranes**

Detailed Description Text - DETX (41):

Preparation of Non-Porous Skinned Asymmetric **Membranes**

Detailed Description Text - DETX (42):

Ground pellets of Hyflon.RTM. (POLY (PTFE-CO-PFVAE)) (Poly (PTFE-CO-PFVAE)) obtained from Ausimont USA, Inc., Thorofare, N.J., were mixed with HaloVac.RTM. 60 from Halocarbon Oil Inc, River edge, N.J. to produce a paste of 40% by weight polymer solids. The polymer/solvent paste mixture is introduced into a heated barrel of a twin screw Baker-Perkins (Saginaw, Mich.) extruder having 29 mm screws. The extruder barrel temperatures were set at between 180.degree. C. and 255.degree. C. A Zenith melt pump (Waltham, Mass.) was used to meter the melt into the special hollow fiber die mentioned above. The die annulus was approximately 300 microns. A low volume flow controller, Brooks Instrument 8744, (Hatfield, Pa.) fed air at controlled rate to maintain the hollow portion of the fiber. The melt pump and air pressure were adjusted to produce a fiber with about a 250 micron thick wall and a 540 micron diameter lumen at a spinning rate of 100 feet per minute. Dioctyl pthalate, maintained at 35.degree. C., was used as the cooling bath. After centering the lumen, the die was operated in the horizontal submerged method. The fiber was taken up on a set of Godet rolls. The fiber was extracted with 1,1-dichloro-1-fluorethane, (Genesolve 2000 Allied-Signal, N.J.) and subsequently dried. The fibers had no observable IPA bubble point up to 100 psi, and no measurable IPA flow. These results indicate that the **membrane** skin was non-porous.

Detailed Description Text - DETX (44):

Production of Microporous Hollow Fiber **Membranes**

Detailed Description Text - DETX (52):

In this example, water is degassed using a **membrane** made in a manner similar to the **membrane** of Example 1. A bundle of fibers was made and potted in a cylindrical holder. The fiber ID was 500.mu. and the fiber wall was about 150.mu. The number of fibers was about 500 and the length of the module was about 20 cm. Water, at a temperature of 20 C., was pumped through the fiber lumens and a vacuum of 60 Torr was maintained on the shell side. The oxygen level of the water was measured at the inlet and outlet of the **membrane**. The inlet water was degassed to a level of 3.1 ppm using a Hoechst Liquid-Cell degasser. The pumping rate was 200 ml/min. and the temp. of water was 20 C. Air at atmospheric pressure was pumped into the shell-side. The airflow rate was about 2 standard liters per minute. The oxygen level at the outlet was observed to rise from 3.1 ppm to 6.8 ppm in a period of 10 min.

Detailed Description Text - DETX (64):

A is the **membrane** area [cm.sup.2].

Detailed Description Text - DETX (73):

The Sherwood and Graetz numbers are dimensionless groups used to describe heat and mass transfer operations. The Sherwood number is a dimensionless mass transfer coefficient, and the Graetz number is a dimensionless group that is related to the inverse of the boundary **layer** thickness. Using the Leveque method, these dimensionless numbers can be correlated. In the linear region, as shown in FIG. 4, the relationship between the Sherwood number and the Graetz number is given as Sh=1.64(Gr).sup.0.33 for Graetz numbers from between about 5 to about 1000. The Leveque method is used to describe heat or mass transfer problems in tubes. In this method, the concentration boundary **layer** is assumed to be confined to a thin **layer** next to the wall of the tube. Yang and Cussler (AICHE J. 32 (11) 1910-1916 (1986)) used this method to correlate mass transfer coefficients for hollow fiber **membrane** contactors. For the case where the liquid was flowing inside the fibers, the Sherwood number followed the relation Sh=A (Gr).sup.b, where A=1.64 and the exponent b=0.33. For this case, they report a range for A as 1.62 to 1.86 from the literature. For liquid flow outside and In cross flow to the fibers, Sh=C(Re).sup.d (Sc).sup.e, where Re is the Reynolds number, dv/.nu., where d=fiber diameter, v=liquid velocity, .nu.=kinematic viscosity, and Sc is the Schmidt number, the ratio of kinematic viscosity to the diffusion coefficient. C has a range of 0.32 to 1.38, d from 0.34 to 0.61 and e is 0.33.

Detailed Description Text - DETX (74):

S. R. Wickramasinghe et al (J. **Membrane** Sci. 69 (1992) 235-250) analyzed oxygen transport in a hollow fiber **membrane** contactor using the method of Leveque. A bundle of porous hollow fiber **membranes** were used. They showed that a plot of the Sherwood number vs. the Graetz number was linear at high values of the Graetz number, in agreement with theoretical predictions. Results at low Graetz number were explained by the polydisperity of fiber diameters, which affects uniformity of flow through the fibers. Their analysis showed that at low Graetz numbers, the average mass transfer coefficient falls below the theoretical prediction due to uneven flow through the fibers. They is concluded that oxygen mass transfer was unaffected by the diffusional resistance across the **membrane**. Conversely, one can conclude that a **membrane** that follows the prediction of the Leveque theory is porous, because otherwise, the resistance to diffusion would be too high to follow the theory.

Detailed Description Text - DETX (75):

The results illustrated in FIG. 7 show that the **membranes** of this example behave as porous **membranes** because they follow the linear portion of the Leveque equation at high Peclet numbers.

Detailed Description Text - DETX (78):

An intrusion test was run on a **membrane** sample produced from a 30% polymer solids solution by a process similar to that described in Example 1. Fiber OD was 750 micron, ID was 485 micron. Isopropyl alcohol was used as the test fluid (surface tension 20.93 mN/m at 25.degree. C.-CRC Handbook of Chemistry and Physics, CRC Press). AT 50 psi, no intrusion was noted after 30 minutes. Some intrusion was noted at 60 psi.

Detailed Description Text - DETX (80):

Preparation of Asymmetric Skinned Perfluorinated Thermoplastic Hollow Fiber **Membrane** with Outside Diameter Skinned

Detailed Description Text - DETX (81):

An asymmetric microporous poly (tetrafluoroethylene-co-perfluoro methyl vinyl ether) ((POLY (PTFE-CO-PFVAE))) hollow fiber **membrane** with a skinned outside surface was prepared by the following method:

Detailed Description Text - DETX (85):

The final fiber is white in appearance and the scanning electron micrographs of its structure are given in FIGS. 9-11. FIG. 10 shows the morphology of the inside (lumen) surface of the fiber and reveals a highly porous structure. FIG. 9 shows the morphology of the outside surface of the fiber and reveals a much denser structure. FIG. 11 shows the morphology of the cross-section of the fiber near the outside surfaces and shows that the tight **layer** on the fiber's outside surface is extremely thin in thickness.

Detailed Description Text - DETX (86):

A practitioner skilled in the art of developing and producing hollow fiber **membranes** will be able to discern the advantages of the present invention. It is not the intent of the discussion of the present invention to exhaustively present all combinations, substitutions or modifications that are possible, but to present representative methods for the edification of the skilled practitioner. Representative examples have been given to demonstrate reduction to practice and are not to be taken as limiting the scope of the present invention. The inventor seeks to cover the broadest aspects of the invention in the broadest manner known at the time the claims were made.

EAST Search History

Ref #	Hits	Search Query	DBs	Default Operator	Plurals	Time Stamp
L1	0	"4553983" "4990225" "4931181" "4963165" "5049167" "5116650" "5281255" "5085775"	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:04
L2	360	210/640.ccls.	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:04
L3	0	perfluoroa dj3 dioxole	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:05
L4	0	perfluoroa dj5 dioxole	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:05
L5	0	perfluoro dj5 dioxole	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:05
L6	541	perfluoro adj5 dioxole	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:05
L7	71	6 and composite membrane	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:06
L8	64	7 and layers	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:06
L9	43	8 and support	USPAT; EPO; DERWENT	AND	ON	2006/09/14 00:06